

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
7 March 2002 (07.03.2002)

PCT

(10) International Publication Number
WO 02/19407 A2

(51) International Patent Classification⁷: **H01L 21/306**

(21) International Application Number: PCT/CA01/01232

(22) International Filing Date: 30 August 2001 (30.08.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/228,770 30 August 2000 (30.08.2000) US
60/244,929 2 November 2000 (02.11.2000) US

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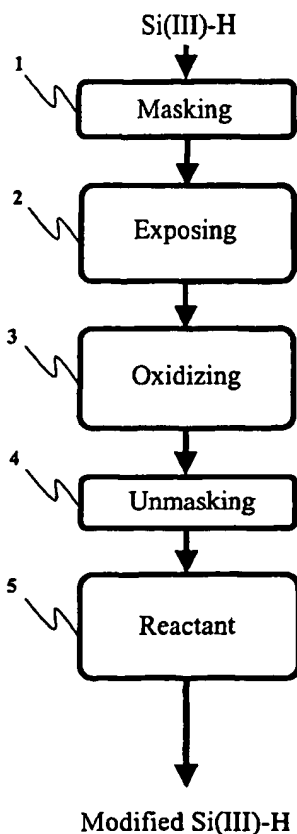
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(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PH, PL, PT, RO, RU, SD, SE, SG, SI,

[Continued on next page]

(54) Title: A METHOD FOR SPATIAL DISTRIBUTION OF CHEMICAL GROUPS ON A SEMICONDUCTOR SURFACE



(57) Abstract: The present invention provides an improved method for the patterning of silicon surfaces. The methods encompass the use of photoinitiation to deliberately oxidize specific regions of a silicon surface, followed by differential modification of the oxidized and non-oxidized portions. In this way, the moieties can be arranged on a silicon surface with accurate spatial organization.

WO 02/19407 A2



SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) **Designated States (regional):** ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— without international search report and to be republished upon receipt of that report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

A METHOD FOR SPATIAL DISTRIBUTION OF CHEMICAL GROUPS ON A SEMICONDUCTOR SURFACE

FIELD OF THE INVENTION

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The present invention relates to the chemical modification of semiconductor surfaces in a spatially resolved manner. More particularly, the invention relates to the chemical modification of semiconductor surfaces to form a monolayer of active molecules arranged in a defined pattern.

10

BACKGROUND TO THE INVENTION

The modification of semiconductor surfaces is required for an increasing number of applications. Generally, these applications require precise spatial distribution of chemical moieties on the semiconductor surface. In this way, chemical groups may be covalently linked to a semiconductor surface in a defined pattern, thereby altering the properties of the surface in a precise manner.

20 Several techniques have been developed to assemble a mono-layer on a semiconductor surface. These techniques generally involve chemical modification of a semiconductor surface comprising hydrogen-terminated silicon (Si(111)-H) (1,2). To initiate monolayer formation, thermal (3), electrochemical (4,5), photochemical (6), and catalytic (7-9) techniques have
25 been developed to covalently link chemical groups to the Si(111)-H surface. Typically, these techniques are used to generate organic monolayers for surface passivation, thereby increasing the chemical stability of the surface.

Importantly, a number of techniques are known that can provide chemical
30 functionality to the semiconductor surface (for examples see references 10 to

13). In this regard, direct chemical patterning enables specific regions of a semiconductor surface to be modified on a micron scale (14-16). Typically, these methods involve photolithographic techniques, piezoelectric printing, or 'drop-touch' binding of materials to the semiconductor surface. In this way, the monolayer can be fabricated into an array of chemical material, wherein regions of differing chemical properties can be arranged with spatial separation in a precisely defined order.

Microarrays have important applications for biochemical analysis. Specifically, semiconductor surfaces can be used to generate microarrays of biological materials (17, 18). Very small samples of biological material can be linked to the semiconductor surface in a precise arrangement. These arrays can be utilized as 'biosensors' for high throughput screening of biochemical activity, for example via spectroscopic or microscopic analysis of the array. Generally, the production of a biomolecular array involves covalent attachment of peptide or nucleotide sequences to the semiconductor surface. The biomolecular arrays generated are sometimes referred to as 'protein chips' and 'gene chips'.

The advent of photoinitiation techniques has provided significant improvements to microarray production and development. Photoinitiation permits direct linkage of groups to hydrogen-terminated semiconductor surfaces (comprising, for example, silicon or germanium) via covalent modification of the surface. The process requires simultaneous application of electromagnetic (EM) radiation, and exposure to a suitable modification chemical.

Importantly, photoinitiation techniques permit selective modification of different regions of the surface (19,20). By masking portions of the surface and preventing exposure to the electromagnetic radiation, the photoinitiation can be directed to other regions of the surface that are not covered by the mask. In this way, photoinitiation techniques can facilitate direct chemical patterning of a

semiconductor surface, thus permitting spatial organization of the chemical properties of the surface.

Typically, the photoinitiation techniques of the prior art involve two
5 photoinitiation steps; each step involving surface modification using a different reactant, wherein the reactants are typically organic compounds. Firstly, a mask is applied to the semiconductor surface, and the partially covered surface is exposed to electromagnetic radiation in the presence of a first reactant. Subsequently, the mask is removed, and any remaining first reactant is washed
10 away. The surface is then re-exposed to electromagnetic radiation in the presence of a second reactant. The regions of the surface that were covered by the mask during the first photoinitiation step are now exposed, and capable of modification by the second reactant. In contrast, the regions modified by the first reactant may be inert to the second reactant, or may undergo differential
15 modification. In any event, the two step photoinitiation process generates a semiconductor surface with chemical properties that are spatially organized.

SUMMARY OF THE INVENTION

20 It is an object of the present invention to provide an improved method for modifying the chemical and physical properties of a surface comprising hydrogen terminated silicon or germanium.

25 It is a further object of the present invention to provide an improved method of preparing a surface for fabrication of a molecular or biomolecular array.

It is a further object of the present invention to provide a technique for photopatterning semiconductor surfaces, that can be carried out in the presence
30 of oxygen.

It is a further object of the present invention to provide a technique for photopatterning semiconductor surfaces, that is not compromised by contamination with oxidants.

5

It is a further object of the present invention to provide a method of generating a silicon or germanium surface with spatially organized chemical properties, wherein only a single photoinitiation step is required.

- 10 It is a further object of the present invention to provide a method of generating a silicon or germanium surface with spatially organized chemical properties, involving multiple photoinitiation steps.

Therefore, in a first aspect, the present invention provides a method of

- 15 covalently modifying a surface comprising hydrogen-terminated silicon or germanium, the method comprising the steps of:

- a) masking a first portion of the surface;
- b) oxidizing a second portion of the surface by exposing the second portion to electromagnetic energy and a source of oxygen or an oxidant, thereby producing an oxide of silicon or germanium;
- 20 c) unmasking the first portion of the surface; and
- d) exposing the surface to a reactant;

- 25 whereby the unmasked first portion of the surface is covalently modified by the reactant and the oxidized second portion of the surface undergoes alternative covalent modification by the reactant, or is unmodified by the reactant.

- In a preferred embodiment of the present invention, the method may further
30 comprise the steps of:

- e) reacting the surface with an agent suitable for converting the silicon or germanium oxide on the second portion of the surface, to hydrogen-terminated silicon or germanium; and
 - f) exposing the surface to a second reactant;
- 5 whereby the second portion of the surface is covalently modified by the second reactant, and the covalently modified first portion of the surface undergoes alternative covalent modification by the second reactant, or is unmodified by the second reactant.
- 10 In another embodiment of the present invention, the method may further comprise modification of the silicon or germanium oxide with an oxide reactant, wherein the portions of the surface that do not comprise silicon or germanium oxide are additionally modified or unmodified by the oxide reactant. In a preferred embodiment, the silicon or germanium oxide is modified with organic
- 15 silanes such as trialkoxysilanes or trihalosilanes. In this way, the regions of the surface comprising silicon or germanium oxide can be selectively modified by the addition of chemical groups suitable for the attachment of molecules such as nucleotides or peptides.
- 20 In a further preferred embodiment, the method of the present invention can permit differential modification of several portions of a silicon or germanium surface by multiple rounds of masking, oxidation, unmasking, and exposure to a suitable reactant, followed by conversion of the remaining oxidized portion of the surface to hydrogen-terminated silicon or germanium. In this way, several
- 25 different chemical groups may be covalently linked to the surface in a precise pattern, whereby the pattern is developed over multiple stages in accordance with the configuration of the masks, and the previously modified portions of the surface.

In a most preferred embodiment, the oxidation step(s) of the methods of the present invention take place in the presence of an oxidant, and in the absence of other reactants.

- 5 The present invention permits fabrication of molecular arrays on a silicon or germanium surface. In particular, the invention is suitable for generating biomolecular arrays of, for example, nucleotide or peptide molecules (including natural or artificial DNA and proteins, or fragments of DNA and proteins). Alternatively, the invention may generate surfaces suitable for the fabrication of
- 10 small molecule arrays.

It is important to note that the method may be used for any application that requires modification of a silicon or germanium surfaces to generate a pattern of differing chemical and physical properties. Typical examples include, but are

15 not-limited to, the production of electric circuits by the deposition of metals, and creation of a pattern for direct chemical or deep reactive ion etching of micron-sized channels for microfluidic circuits or micro-electro-mechanical systems (MEMS) devices.

20

BRIEF DESCRIPTION OF THE DRAWINGS

- Figure 1** is a flow chart of one embodiment of the method of the present invention, wherein the silicon surface is modified by a single reactant.
- 25 **Figure 2** is a flow chart of a preferred embodiment of the method of the present invention, wherein the silicon surface is modified by two reactants.
- Figure 3** is a flow chart of a preferred embodiment of the method of the present invention, wherein the silicon surface is modified by more than two reactants.
- Figure 4** is a schematic diagram to illustrate selective modification of a portion
- 30 of a silicon surface in accordance with the method of the present invention.

Figure 5a is a tapping mode atomic force microscopy (AFM) image of a gold minigrid mask, suitable for use in accordance with the method of the present invention ($140\mu\text{m} \times 140\mu\text{m}$).

Figure 5b is a charged couple device (CCD) image of a patterned Si(111) surfaces after exposure to water vapour revealing a pattern of 160,000 SiO_2 'pads' per cm^2 .

Figure 5c is an atomic force microscopy (AFM) height image of a patterned Si(111) surface ($140\mu\text{m} \times 140\mu\text{m}$).

Figure 5d is a atomic force microscopy (AFM) frictional force image of a patterned Si(111) surface using an unmodified silicon nitride tip ($140\mu\text{m} \times 140\mu\text{m}$).

Figure 6a is a field emission-scanning electron micrograph of a patterned silicon surface generated in accordance with the present invention.

Figure 6b is a scanning auger electron spectroscopy (SAES) line scan of the modified surface shown in Figure 6a, depicting the relative abundance of carbon (solid line) and oxygen (dashed line) as a function of distance (for example across line A-A' in Figure 6a).

Figure 7 is a scanning laser confocal microscope image of a protein chip generated in accordance with the method of the present application.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The method of the present invention provides an improved technique for modifying the chemical and physical characteristics of a silicon or germanium surface. In this way, the surface may be altered so that neighboring regions exhibit entirely different properties. Moreover, the present invention permits the application of a pattern of chemical modification on a micron scale.

Importantly, the method involves fewer chemicals, and may be carried out without the requirement for an oxygen / oxidant free environment.

Whilst the present invention will be described with particular reference to Si(111) surfaces, the methods may be applied to any silicon or germanium semiconductor surface. Both silicon and germanium exhibit very similar
5 chemical properties, and chemical modification of these surfaces by photoinitiation, thermal or catalytic mechanisms is expected to occur by similar, if not identical mechanisms. Therefore, the present invention encompasses methods for the modification of any silicon or germanium surface in accordance with the teachings provided herein. Silicon surfaces are preferred, since the low
10 cost of silicon relative to the cost of germanium will reduce the overall production costs of the patterned surfaces. Moreover, silicon surfaces are particularly preferred when the reaction steps require a high degree of oxide stability. In this regard, silicon oxide is considerably more stable than germanium oxide. Hydrogen-terminated Si(111) is a particularly preferred
15 substrate, since this form of silicon is known to form very flat and uniform surfaces, which are especially suited to the inventive methods disclosed herein.

The inventors of the present invention have discovered that silicon oxidation can be utilized to provide significant improvements in chemical patterning.
20 Specifically, the present invention teaches a method wherein a semiconductor surface (preferably a Si(111)-H surface) is deliberately exposed to electromagnetic radiation in the presence of oxygen or an oxidant. Regions of the surface that are masked from the electromagnetic radiation retain their original hydrogen-termination, whereas regions that are exposed to the
25 electromagnetic radiation become oxidized. Following this initial oxidation step, the oxidized and non-oxidized regions of the surface can undergo alternative chemical modification. Preferably, the electromagnetic radiation is ultraviolet radiation, and more preferably, the electromagnetic radiation has a wavelength between 150nm and 350nm.

Advantageously, the method of the present invention permits single or multiple rounds of covalent modification. Therefore, the invention encompasses embodiments that permit a single covalent modification of the silicon surface, wherein desirable properties are conferred to the surface using a single
5 photoinitiation step. Alternatively, the method may be extended to provide a method for binding two or more different chemical species to the silicon surface, confined to spatially distinct and separated regions of the surface.

The embodiments of the method described herein permit modification of a
10 semiconductor surface comprised substantially of hydrogen-terminated Si(111) (hereinafter termed Si(111)-H). In this regard, the Si(111)-H surface may be prepared by any of a number of techniques that are well known in art. The surface can be cleaned (for example with a piranha solution of 3:1 $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2$), and subsequently reduced by reaction with a suitable reducing
15 agent (for example NH_4F).

A first embodiment of the present invention is described with reference to Figure 1, which outlines a method involving a single photoinitiation step. In a first stage 1, the Si(111)-H surface is masked by a suitable mask. The mask
20 may comprise any material that blocks subsequent access of electromagnetic radiation to the Si(111)-H surface. In preferred embodiments of the present invention, the mask may comprise a metallic element, alloy or composition. Particularly preferred materials include chromium, aluminum, and gold. Alternatively, the mask may comprise glass or fused silica, with metals
25 deposited on the surface of the glass or fused silica. The mask may be in physical contact with the surface, or in close proximity to the surface. Moreover, the mask is preferably configured to define the regions of the surface that will be subsequently modified by a reactant.

- After the mask is located in a desirable position relative to the surface, the surface is radiated with electromagnetic energy in a second step 2. Importantly, the reaction takes place in the presence of oxygen (or air), and/or in the presence of a suitable chemical oxidant. In this way, the regions of the surface that are exposed to the electromagnetic radiation (and not covered by the mask) become selectively oxidized by photoinitiation, thereby generating a silicon oxide pattern on the surface in step 3. In a preferred embodiment, the oxidant utilized for the photoinitiation step 2 is air. In this way, the photoinitiation step is effectively 'reagentless', in that the patterning may be carried out in air without the need for additional chemical reagents. This feature presents a significant practical advantage to the methods of the present invention, since organic reagents do not need to be present in the vicinity of sensitive lithographic instruments.
- 15 —Following oxidation, the mask is removed in step 4, and the silicon surface previously covered by the mask is exposed. This region of the silicon surface remains hydrogen terminated, since it was concealed from photoinitiation by the mask. In step 5, the silicon surface may then be exposed to a reactant capable of covalently modifying the remaining Si(111)-H surface (initially covered by the mask). The covalent modification reaction may be facilitated by an input of thermal energy to heat the reactant in the presence of the surface. In this regard, the reactant may preferably be selected from the group consisting of an alkene, an alcohol, and aldehyde, a thiol, an alkenyl, and a Grignard reagent. Alternatively, the reaction may be induced by the addition of a suitable catalyst, or by photoinitiation in a similar manner to that described for step 2.

The reactant used in step 5 may be any reactant capable of reacting with Si(111)-H to confer desirable properties to the surface. For example, the reactant may be an alkene terminated with ethylene glycol, which can modify the surface in a manner suitable for the subsequent linkage of protein or

peptides to the silicon. In another example, the reactant may be an alkene terminated with a nitrophenylester, which can provide useful covalent modification of the surface for multiple rounds of surface modification. In this regard, the ester bond of the nitrophenylester can be disrupted to generate a
5 carboxylic acid attached to the surface for subsequent surface modification at a position remote from the silicon.

Optionally, the method shown in Figure 1 may further comprise modification of the silicon oxide (not indicated in Figure 1). In this regard, the surface may be
10 exposed to a reagent that specifically reacts with the silicon oxide. For example, the silicon oxide may be modified by exposure of the surface to a trialkoxysilane or trihalosilane comprising a suitably reactive end group for subsequent attachment of nucleotide or peptide molecules to the surface. In this way, the method illustrated in Figure 1 can be adapted to permit facile
15 immobilization of DNA or proteins over the silicon oxide regions, thereby allowing fabrication of a biomolecular array. Alternative modifications of the silicon oxide may permit direct linkage of a small molecule array, as required. In an alternative embodiment, the optional modification of the oxidized silicon surface may comprise soft lithography or micro-contact printing (reviewed in
20 21).

Therefore, in accordance with the method outlined in Figure 1, the Si(111)-H surface is chemically modified via an initial photoinitiation step to partially oxidize the surface, wherein the surface ultimately comprises regions of silicon
25 oxide spatially separated by regions of silicon covalently modified by a suitably chosen reactant.

In a preferred embodiment, the step of masking may involve the use of a grid-like mask, wherein the holes in the grid define the portions of the surface that
30 become oxidized. In this way, the method will generate a surface patterned

with an ordered array of oxidized silicon, wherein the array comprises a series of 'pads' of silicon oxide arranged in rows and columns. This configuration of the silicon oxide patterning is particularly suited for the fabrication of a molecular array, wherein different molecules are covalently linked to adjacent silicon oxide 'pads' of the array. For example, the 'pads' of silicon oxide may be selectively chemically modified with a trialkoxysilane or a trihalosilane, thereby rendering the silicon oxide 'pads' receptive to the addition of peptide or nucleotide molecules. Subsequently, specific molecules may be 'spotted' onto each position of the array via techniques that are known in the art, for example involving the use of robotic arrayer devices (for example see 22).

An alternative embodiment of the present invention is illustrated in Figure 2. This embodiment extends the embodiment illustrated in Figure 1, to provide a method of covalently modifying a Si(111)-H surface using two different reactants. The initial steps of the procedure (steps 1-5) are as described for Figure 1. However, the end product of the method shown in Figure 1 undergoes two additional processing steps 6 and 7 (Figure 2). These additional steps permit the conversion of the oxidized silicon to a surface covalently modified by a second reactant.

In accordance with the embodiment shown in Figure 2, the silicon oxide generated in the initial photoinitiation step is reduced to regenerate Si(111)-H in step 6. For this purpose, any reducing agent may be utilized with the capacity to instigate conversion of the silicon oxide to Si(111)-H. Preferably, the reducing agent should not confer undesirable changes to those regions of the surface modified at step 5. For example, if the silicon surface is alkylated at step 5, then HF would constitute a suitable reducing agent, since the alkylated silicon will not react with HF. Moreover, HF is a preferred reducing agent for most applications. An alternative example of a suitable reducing agent is KOH.

However, KOH is generally less preferred since KOH may react adversely with other chemical moieties present on the surface.

After the silicon oxide has been converted back to Si(111)-H, the newly regenerated Si(111)-H undergoes covalent modification using a suitably chosen reactant at step 7. In this regard, the reaction between the Si(111)-H and the reactant at step 7 may be induced by heating the surface and the reactant, by the addition of a catalyst, or by photoinitiation. Moreover, the reactant may be selected to confer additional modifications to regions of the surface covalently modified in a previous step. In any event, the end product comprises a silicon surface that has been modified by two different reactants. The oxidation step 3 facilitates the differentiation of distinct regions of the silicon surface, which subsequently undergo alternative chemical modification using the two different reactants at steps 5 and 7.

15 —————

In an alternative embodiment of the present invention, the method illustrated in Figure 2 may be adapted and extended to permit covalent modification using three or more different reactants. This embodiment is described with reference to Figure 3. The method is similar to the embodiment shown in Figure 2, and additionally includes a feedback loop 8. This feedback loop defines a method wherein steps 1 through 6 may be repeated as many times as required.

The surface at step 6 (Figure 3) comprises a region of silicon covalently modified by a first reactant and a region of Si(III)-H (regenerated by the reduction of silicon oxide). In accordance with feedback loop 8, a mask is applied to the silicon surface at step 1. The configuration of the mask may differ from that of the original mask used for the first photoinitiation step. In this way, subsequent oxidation of the surface by photoinitiation (steps 2 and 3) generates an alternative pattern of oxidation compared to the first photoinitiation reaction. At step 4, the mask is removed, to expose the

remaining Si(111)-H. It is important to note that the regions of remaining Si(111)-H are defined both by the regions of newly oxidized silicon, and also by the regions of the surface that have already been modified by a previous reactant (e.g. from the first round of modification).

5

Subsequently, the remaining regions of Si(111)-H undergo chemical modification with a suitably chosen reactant at step 5. In this regard, the reaction between the Si(111)-H and the new reactant may be induced by thermal, catalytic or photoinitiation mechanisms to effect the desired
10 modification. Moreover, the reactant may be selected to confer additional modification to regions of the surface covalently modified in a previous step, as required.

Although not indicated in Figure 3, the remaining regions of oxidized silicon
15 may be modified at this stage by a suitable oxide reactant (as described having regard to the embodiment illustrated in Figure 1). In this case, the end product is a silicon surface comprising three modifications: two resulting from covalent modification of Si(111)-H with two different reactants, and the third comprising silicon oxide (or modified silicon oxide, as required). Alternatively, as shown
20 in Figure 3 the regions of the surface comprising newly oxidized silicon may be converted back to Si(111)-H using a suitable reducing agent (at step 6). At this stage, if the surface will be modified only by one further reactant, then the surface is exposed to the reactant (with thermal, catalytic or photoinitiation, as required), to effect the final modification of the surface at step 7. In this case,
25 the end product is a silicon surface comprising a pattern of three alternative chemical modifications, each located in spatially distinct regions of the surface.

The present invention also encompasses a method wherein a silicon surface is subjected to multiple rounds of modification. Therefore, as shown in Figure 3,
30 the feedback loop 8 of steps 1 to 6 may be repeated many times, each involving

a different reactant, thereby generating a silicon surface with a complex pattern of many chemical moieties with a range of desired properties. As described previously, regions of oxidized silicon may be left on the surface, or may be removed with HF and filled in with a final reactant, or alternatively may be
5 modified with a silicon oxide specific reactant, as required.

Whilst the photoinitiation methods of the prior art may also permit multiple rounds of photoinitiation, the provision of the oxidation steps of the present invention confer several distinct advantages. Firstly, silicon oxide is relatively
10 inert, and therefore less likely to be involved in side reactions with the reactants. Secondly, without wishing to be bound by theory, it is believed that the methods of the present invention provide significant improvements with regard to chemical modification efficiency. In accordance with the methods of the prior art, slight oxidant contamination can significantly reduce the efficiency of
15 chemical modification and compromise the desirable electrical properties of the silicon. For this reason, one may expect that the level of unwanted Si(111)-H oxidation to increase for each round of chemical modification. In contrast, the present invention utilizes silicon oxidation to an advantage, thereby circumventing problems relating to oxidant contamination.

20
Importantly, the methods of the present invention permit the steps of photoinitiation, and reactant-induced covalent modification, to be temporally separated. For this reason, a reactant may be selected that is capable of modifying Si(111)-H in the absence of photoinitiation. Alternatively, a
25 photoinitiation-dependent reactant may also be used, as appropriate. In this way, the range of suitable reactants is not limited to those amenable to photoinitiation.

A further advantage of the present invention relates to the generation of silicon
30 oxide. For some applications, it may be convenient to leave the oxide layer

intact, and subsequently react the oxidized silicon surface as appropriate. Such modifications of the silicon oxide could themselves impose useful properties to the silicon oxide. For example, reaction of the silicon oxide with alkyl trialkoxysilanes or alkyl trichlorosilanes can alter the hydrophobicity of these regions of the silicon surface, and introduce new reactive groups with high spatial fidelity. In an alternative example, the provision of amines or aldehydes can serve as attachment sites for nucleotide and peptide molecules.

The following examples relate to the use of a method of the present invention to generate a silicon surface suitable for the fabrication of an array of biomolecular material. However, it is important to note that the methods of the present invention may be applied to any system that requires chemical modification of a silicon surface in a spatially organized manner.

Example 1

This example illustrates the capacity of the methods of the present invention, to confer distinct chemical properties to a silicon surface with spatial organization on a micron scale. The steps of the method are illustrated schematically in Figure 4, wherein the Si(111)-H surface is modified with 1-decene.

The surface of a silicon wafer was pretreated with a piranha solution of 3:1 $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2$ at 80°C for 30 minutes before immersion in a deoxygenated aqueous NH_4F solution for 15 minutes to form a hydrogen-terminated silicon surface. The freshly prepared Si(111)-H surface was pressed against an electroformed gold mask (Buckbee-Mears), which was a grid of ca. 10µm diameter wires with a centre to centre spacing of 25µm. The Si(111)-H surface was exposed through the mask using a pen lamp (254nm) in ambient air for 30 minutes. The sample was removed, immersed in deoxygenated 1-decene and

irradiated (300nm) for 3 hours. This step initiated a hydrosilylation reaction between the hydrogen-terminated surface (the part that was masked to ultraviolet radiation by the gold mask), and the 1-decene. The wafer was then rinsed with THF and 1,1,1-trichloroethane to remove any physisorbed hydrocarbons from the surface.

Example 2

An AFM image of the gold mask utilized in Example 1 is shown in Figure 5a.

10

The chemically modified silicon wafer generated in Example 1 was subsequently exposed to water vapour. An optical image of the wafer revealed a well ordered pattern of water distribution on the surface of the wafer (Figure 5b), with the silicon oxide (squares) being hydrophilic and the 1-decene modified surfaces (lines) being hydrophobic. Therefore, the surface of the silicon wafer had effectively been fabricated into an array of 'pads' of silicon oxide with a density of about 160,000/cm². The surface of the wafer exhibited altered surface tension with an accuracy of at least a few tens of microns. These results highlight the implications of the methods of the present invention for use in microarray and electronic applications.

20

An AFM height image was also generated for the surface of the wafer (Figure 1c). This image shows that the organic surface modified by 1-decene is topographically higher than the silicon oxide (with an estimated height gain of approximately 10Å). The contrast is further improved in the frictional force image (Figure 1d), in which the hydrophilic nature of the silicon oxide squares is evident.

25

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Claims:

1. A method of covalently modifying a surface comprising hydrogen-terminated silicon or germanium, the method comprising the steps of:

5

- a) masking a first portion of said surface;
- b) oxidizing a second portion of said surface by exposing said second portion to electromagnetic radiation and a source of oxygen or an oxidant, thereby producing silicon or germanium oxide;
- c) unmasking said first portion of said surface; and
- d) exposing said surface to a reactant;

10

whereby said first portion of said surface is covalently modified by said reactant and said oxidized second portion of said surface undergoes alternative covalent modification by said reactant, or is unmodified by said reactant.

15

2. A method according to claim 1, wherein said silicon or germanium is Si(111), and said silicon or germanium oxide is oxidized Si(111).

20

3. A method according to claim 1, further comprising the step of chemically modifying said silicon or germanium oxide with an oxide reagent to confer desirable properties to said second portion of said surface.

25

4. A method according to claim 3, wherein said chemical modification of said silicon or germanium oxide comprises soft lithography or micro-contact printing.

5. A method according to claim 3, wherein said oxide reagent is a trialkoxysilane or a trichlorosilane, and said second portion of said surface exhibits increased hydrophobicity.
- 5 6. A method according to claim 3, wherein said oxide reagent modifies said second portion of said surface for subsequent attachment of molecules.
7. The method according to claim 6, wherein said molecules are selected from the group consisting of peptides and nucleotides.
- 10 8. A method according to claim 1, wherein said silicon or germanium oxide is not modified by said reactant.
9. A method according to claim 1, wherein said silicon or germanium
15 oxide is modified by said reactant.
10. A method according to claim 1, wherein said reactant is an alkene terminated with ethylene glycol.
- 20 11. A method according to claim 1, wherein said reactant is an alkene terminated with a nitrophenylester.
12. A method according to claim 1, wherein said source of oxygen or oxidant comprises air.
- 25 13. A method according to claim 1, wherein step d) is induced by photoinitiation comprising exposure of said surface to electromagnetic radiation.

14. A method according to claim 13, wherein step d) comprises exposure of said surface to ultraviolet radiation.
15. A method according to claim 13, wherein said electromagnetic radiation
5 has a wavelength of from 150nm to 350nm.
16. A method according to claim 1, wherein step d) is induced by heating said surface with said reactant.
- 10 17. A method according to claim 1, wherein step d) is induced by addition of a catalyst.
18. A method according to claim 1, wherein said electromagnetic radiation comprises ultraviolet radiation.
15
19. A method according to claim 1, wherein said electromagnetic radiation has a wavelength of from 150nm to 350nm.
20. A method according to claim 16, wherein said reactant is selected from
20 the group consisting of an alkene, an alcohol, an aldehyde, a thiol, an alkenyl, and a Grignard reagent.
21. A method according to claim 1, wherein step a) comprises masking said surface with a mask.
25
22. A method according to claim 21, wherein said mask comprises a metal, or an alloy.
23. A method according to claim 22, wherein said mask comprises a metal
30 selected from the group consisting of chromium, aluminum and gold.

24. A method according to claim 22, wherein said mask comprises glass or fused silica, and said metal is deposited on said glass or fused silica.
- 5 25. A method according to claim 21, wherein said mask is a grid, and said method generates an array of silicon or germanium oxide on said surface, said array comprising elements of silicon or germanium oxide.
26. A method according to claim 25, wherein said elements are chemically
10 modified such that each element of said array is modified differently.
27. A method according to claim 25, further comprising the step of covalently linking DNA molecules to said elements to generate a biomolecular array comprising DNA.
15
28. A method according to claim 25, further comprising the step of covalently linking peptide molecules to said elements to generate a biomolecular array comprising peptides.
- 20 29. A method according to claim 25, further comprising the step of covalently linking small molecules to said elements.
30. A method according to any one of claims 1 to 29, further comprising the steps of:
25
- e) reacting said surface with an agent suitable for converting said silicon or germanium oxide on said second portion of said surface, to hydrogen-terminated silicon or germanium; and
 - f) exposing said surface to a second reactant;
- 30

whereby said second portion of said surface is covalently modified by said second reactant, and said covalently modified first portion of said surface undergoes alternative covalent modification by said second reactant, or is unmodified by said second reactant.

5

31. A method according to claim 30, wherein said first portion of said surface is unmodified by said second reactant.

32. A method according to claim 30, wherein said first portion of said
10 surface is modified by said second reactant.

33. A method according to claim 30, wherein step f) is induced by photoinitiation comprising exposure of said surface to electromagnetic radiation.

15

34. A method according to claim 33, wherein said electromagnetic radiation comprises ultraviolet radiation.

35. A method according to claim 33, wherein said electromagnetic radiation
20 has a wavelength of from 150nm to 350nm.

36. A method according to claim 30, wherein step f) is induced by heating said surface with said reactant.

25 37. A method according to claim 30, wherein step f) is induced by addition of a catalyst.

38. A method according to claim 30, wherein said agent comprises HF.

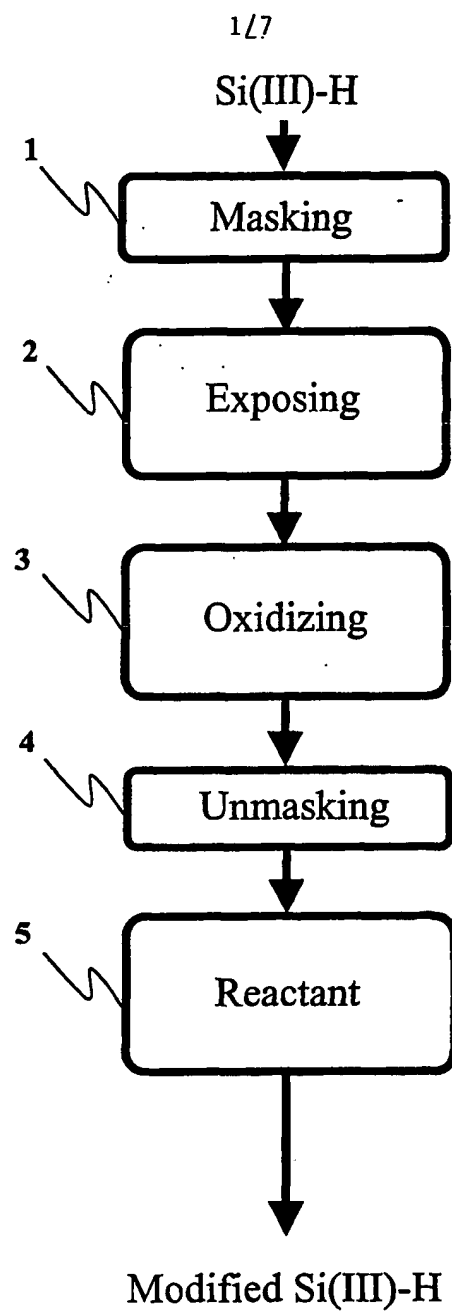
30 39. A method according to claim 30, wherein said agent comprises KOH.

40. A method according to any one of claims 30 to 39, wherein steps a) to e) are repeated using different reactants as required.

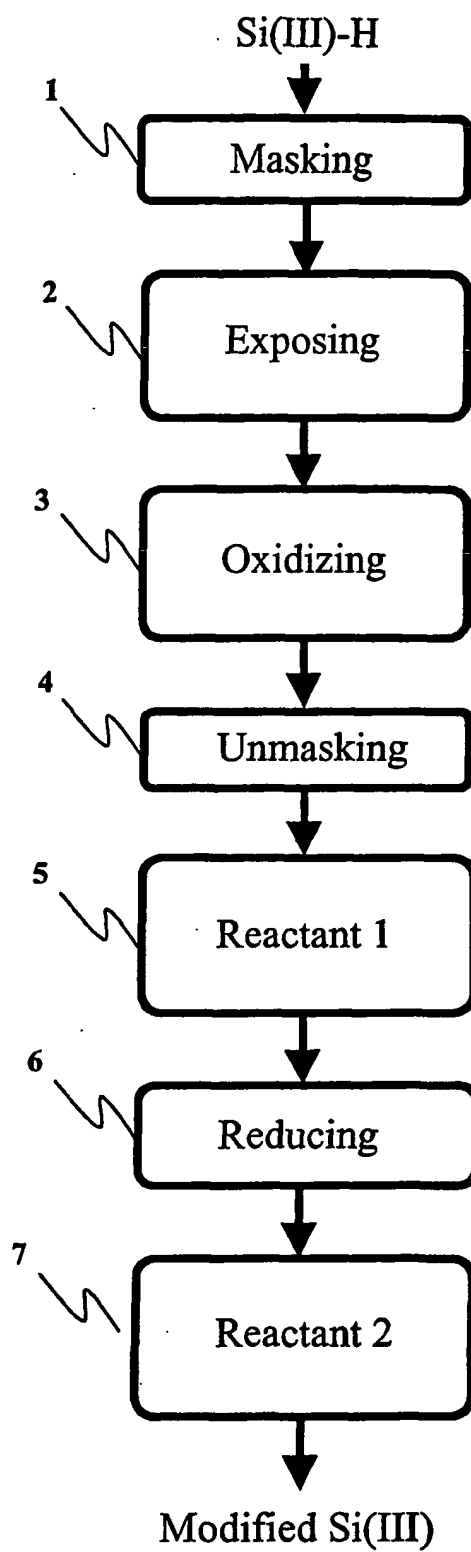
41. A method according to claim 40, wherein a portion of said silicon or
5 germanium oxide, or said modified silicon or germanium oxide remains on said surface.

10

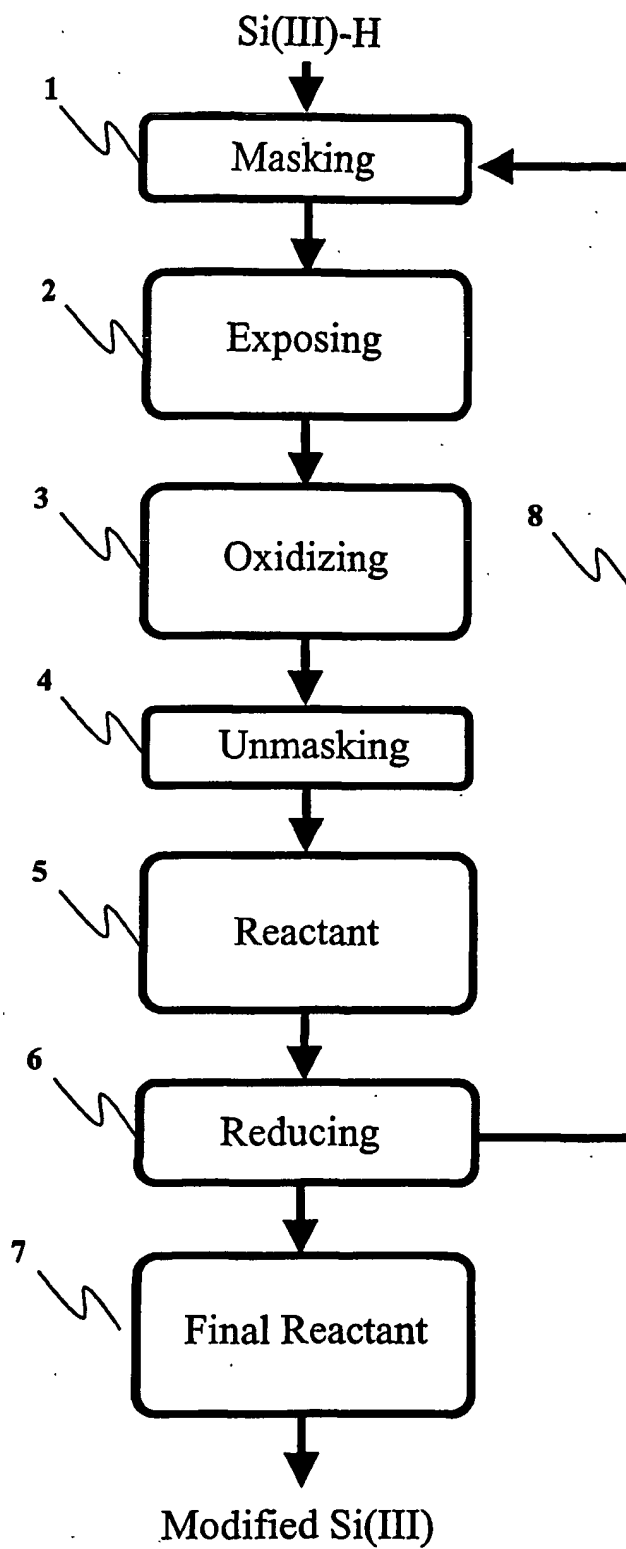
15

**Figure 1**

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**Figure 2**

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**Figure 3**

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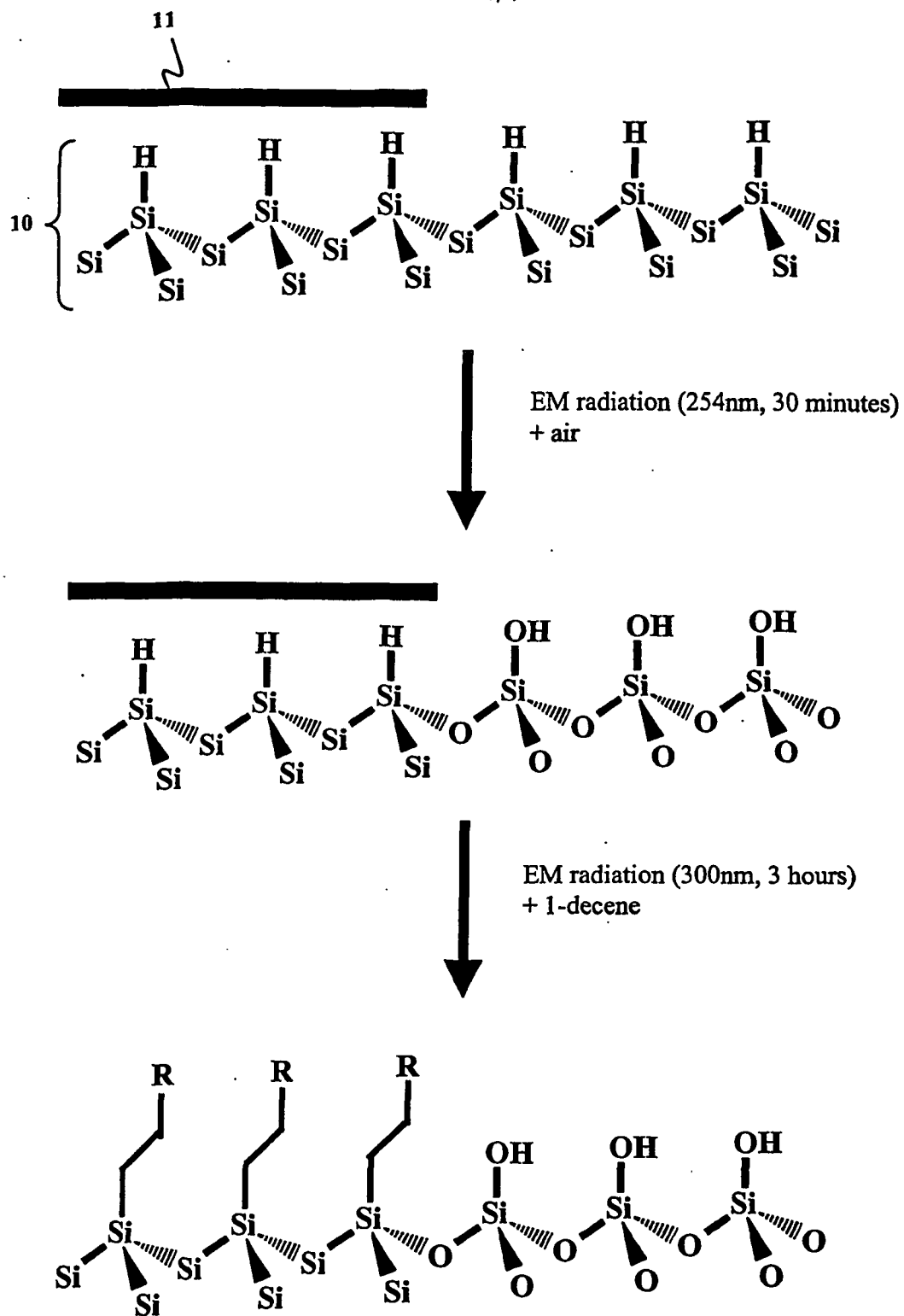


Figure 4

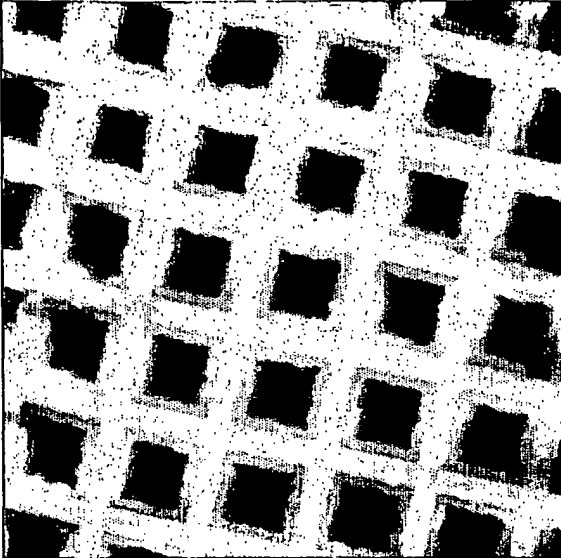


FIG. 5a

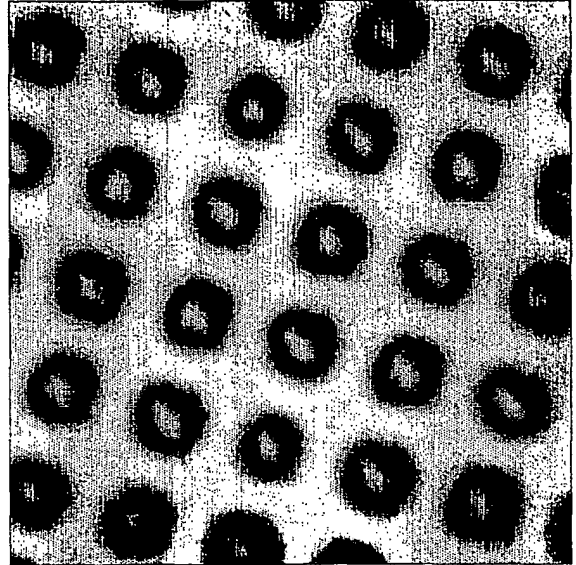


FIG. 5b

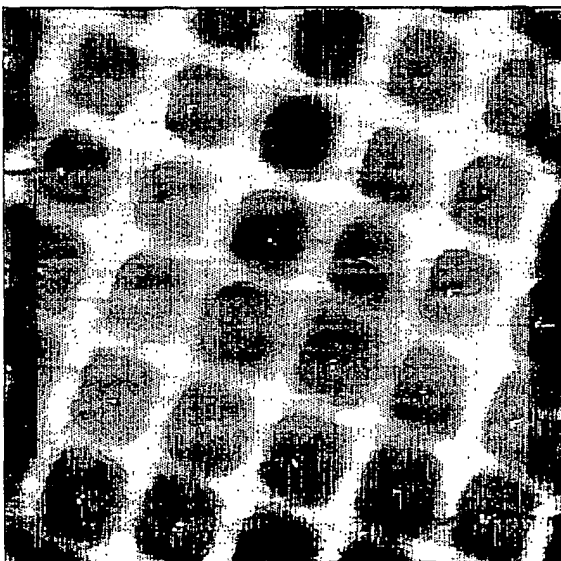


FIG. 5c

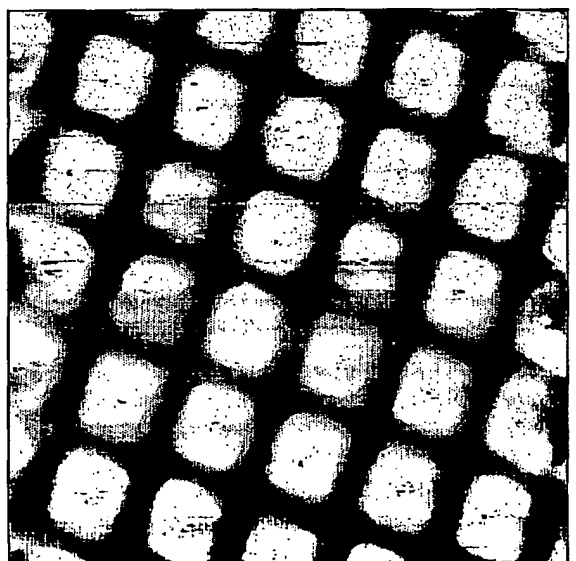
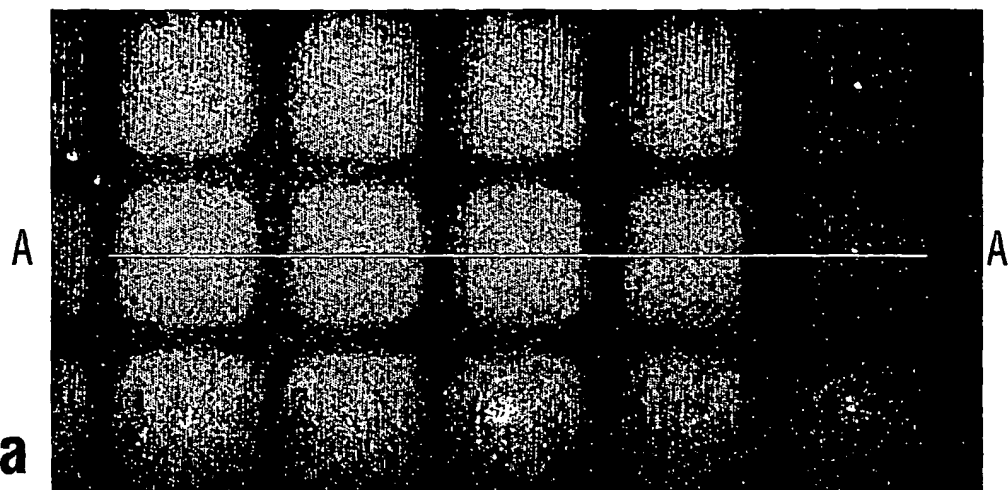
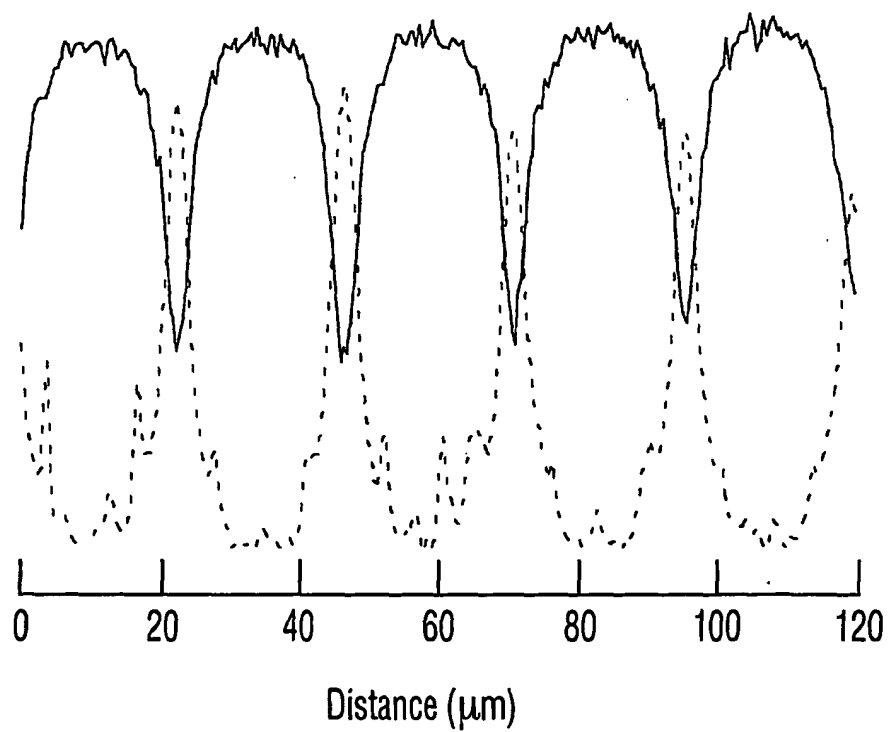


FIG. 5d

FIG. 6a**FIG. 6b**

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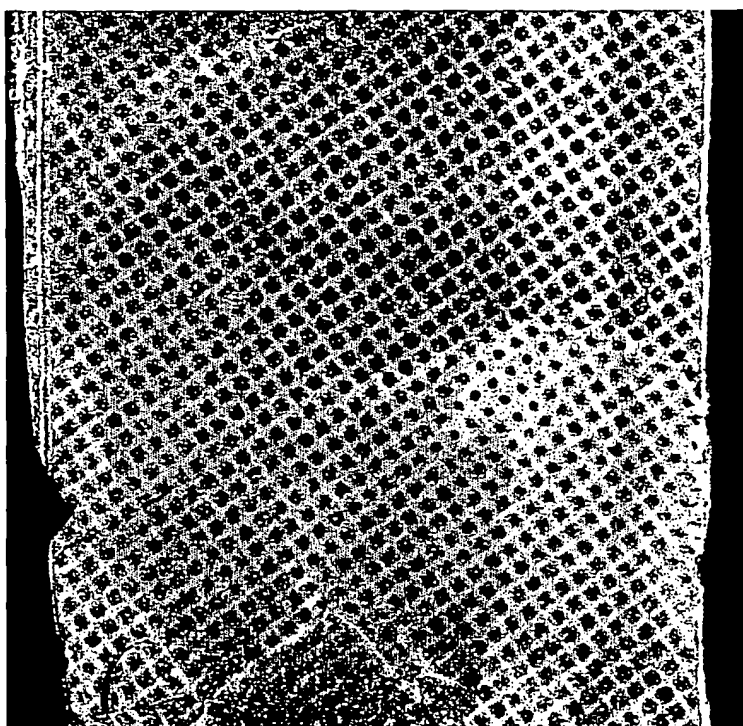


FIG. 7

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
7 March 2002 (07.03.2002)

PCT

(10) International Publication Number
WO 02/019407 A3

(51) International Patent Classification⁷: **G01N 33/50**,
H01L 21/306

(21) International Application Number: PCT/CA01/01232

(22) International Filing Date: 30 August 2001 (30.08.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/228,770 30 August 2000 (30.08.2000) US
60/244,929 2 November 2000 (02.11.2000) US

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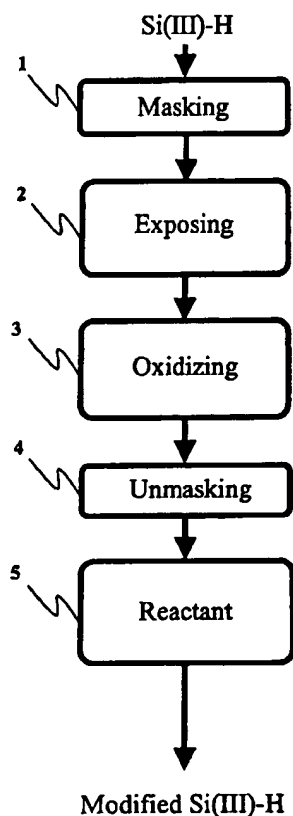
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(81) Designated States (national): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,
CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,
GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,
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MX, MZ, NO, NZ, PH, PL, PT, RO, RU, SD, SE, SG, SI,

[Continued on next page]

(54) Title: A METHOD FOR SPATIAL DISTRIBUTION OF CHEMICAL GROUPS ON A SEMICONDUCTOR SURFACE



(57) Abstract: The present invention provides an improved method for the patterning of silicon surfaces. The methods encompass the use of photoinitiation to deliberately oxide specific regions of a silicon surface, followed by differential modification of the oxidized and non-oxidized portions. In this way, the moieties can be arranged on a silicon surface with accurate spatial organization.



WO 02/019407 A3



SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU,
ZA, ZW.

Published:

— with international search report

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

(88) Date of publication of the international search report:
19 September 2002

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INTERNATIONAL SEARCH REPORT

Interl nal Application No

PCT/CA 01/01232

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 G01N33/50 H01L21/306

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 G01N H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Date of the actual completion of the international search

12 June 2002

Date of mailing of the international search report

24/06/2002

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